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Relationship Between Residual Lignin Structure and Pulp Bleachability

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RELATIONSHIP BETWEEN RESIDUAL LIGNIN STRUCTURE AND PULP BLEACHABILITY

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ABSTRACT

Efficient use of ClO_2 during ECF chemical pulp bleaching is an important concern for mills employing such bleaching technology. Efficient use requires a fundamental understanding about the reactions of ClO_2 with residual lignin. The objective of this study was to define a relationship between unbleached residual lignin structure and pulp bleachability during a D(EO) sequence. This has been accomplished by extensively characterizing the residual lignin structure in a series of unbleached conventional and EMCC[®] kraft pulps and relating this structure to measures of bleachability. Additionally, functional group changes in residual lignins isolated from these chemical pulps and treated with chlorine dioxide have been related to the measures of bleachability.

Results from this study suggest that although free phenolic structures are believed to be the main site of attack by ClO_2 , their content in the unbleached residual lignin cannot simply be related to the observed bleaching response. Lower kappa number pulps were found to contain a greater content of free phenolic structures yet the bleaching experiments, in general, found that as the kappa number is decreased there is a slight increase in TAC consumption per unit kappa number reduction in the D(EO) sequence. Reactivity studies of ClO_2 with residual lignin suggest that residual lignin in higher kappa number pulp is more reactive towards ClO_2 , which is consistent with the observed bleaching response. Additional structural differences between these unbleached residual lignins include the content of aryl ether linkages and the amount of condensed aromatic units. How these structural features may relate to the observed bleaching response is discussed.

INTRODUCTION

Efficient delignification during ECF bleaching is believed to be significantly influenced by the reactivity of residual lignin towards chlorine dioxide. The structure of residual lignin should play a key role in this reactivity, particularly the content of free phenolic groups, which have already been shown to have an effect on ClO_2 delignification (1). The structure of residual lignin in unbleached kraft pulps is believed to be influenced by both pulping process variables and the extent of delignification (2,3,4), suggesting that residual lignins will have different reactivities towards ClO_2 , depending upon how the pulp was produced. However, a clear relationship between residual lignin structure and pulp bleachability has not yet been established.

In this study, we elected to determine how the extent of delignification and pulping process variables (conventional vs. EMCC[®] kraft pulping) affect the bleachability of kraft pulps during a D(EO) delignification sequence and to relate observed bleachability differences to differences in residual lignin structure. Residual lignin structure was characterized by applying advanced nuclear magnetic resonance (NMR) methods.

EXPERIMENTAL

Kraft Pulping

The kraft pulping experiments were performed at Kamyr's pilot facilities in Glens Falls, NY. Established procedures were used to simulate conventional and EMCC[®] kraft pulping (5). The chip source used for all pulps was a *Pinus taeda* tree cut in north Georgia, USA. This tree was debarked, chipped and carefully screened (chip thickness was between 2 and 6 mm). Table 1 lists the pulping conditions used and properties of the pulps.

Table 1. Relevant pulping conditions and pulp properties from the conventional and EMCC[®] kraft pulps.

Cook Type	Conventional Kraft			EMCC [®]		
Pulp ID	C28	C18	C13	E29	E18	E14
Initial EA, % NaOH	19.7	19.7	22.0	12.0	12.0	12.0
Co-Current EA charge, %	0.0	0.0	0.0	5.0	5.0	5.0
Max.Temp., °C	170.0	170.0	170.0	157.5	161.0	168.6
H-Factor	1715	2601	4238	1651	2229	4238
Kappa Number	28.0	18.5	13.0	29.1	18.5	14.5
Viscosity, mPa.s	33.6	17.5	10.9	51.8	35.4	18.1
V/K ratio	1.20	0.95	0.84	1.78	1.91	1.25
Screened Yield, %	45.9	42.8	41.0	45.6	43.8	40.9

All cooks employed white liquor having a sulfidity of 27.4%. Pulp ID's are designated by the first letter of the cook type followed by the kappa number.

Bleaching

The D stage bleaching was performed in a Quantum Technologies mixer at 45°C and 10% consistency for 30 minutes at a kappa factor of 0.187 ± 0.05 . The (EO) stage was done in a peg mixer at 70°C and 10% consistency for 60 minutes with a charge of sodium hydroxide corresponding to 50% of the D total active chlorine (TAC) charge. The O₂ pressure was 60 psig initially and was decreased by 12 psi every 5 minutes.

Residual Lignin Isolation

Residual lignin was isolated from the various pulps by employing an improved version of an acid hydrolysis procedure that has frequently been used in the literature to isolate lignin from both wood and pulp (8,9,10). The pulp was refluxed for one hour in a 9:1 mixture of dioxane:water with an HCl concentration of 0.05N. The dissolved lignin was collected by removing the dioxane and recovering the precipitate after acidifying the aqueous solution to a pH of 2.5. The yield of lignin ranged from 30 to 45% based on the theoretical amount of lignin in pulp as determined by the kappa number/klason lignin relationship (% Klason lignin = $0.15 \times \text{kappa number}$).

Residual Lignin Reactivity Experiments with ClO₂

Dried residual lignin (80.0 mg) was accurately weighed and placed in a small reaction flask. A purified dioxane:water (9:1) solvent mixture was added to each of the residual lignins until dissolved (25.0 ml). A charge of aqueous ClO₂ was then added to the reaction flask. (The aqueous ClO₂ was made carefully so an insignificant amount of Cl₂ was present in the ClO₂ solution). The reaction was allowed to proceed for 30 minutes at room temperature. After the reaction, a 1.0 ml aliquot of the solution was titrated for residual ClO₂. The reaction was terminated by bubbling nitrogen through the solution for 30 minutes under vacuum to remove unreacted ClO₂. The solution was then freeze-dried and the recovered product analyzed by quantitative ³¹P-NMR spectroscopy. For the 0.05 kappa factor experiments, 0.127 grams of ClO₂ was added per gram of residual lignin.

Quantitative ³¹P-NMR

Quantitative ³¹P-NMR spectroscopy was used to analyze the residual lignins following literature protocol (6). Briefly, 25 mg of lignin was accurately weighed and dissolved in 400 uL of a 1.6:1 solvent mixture of pyridine:chloroform-d. An internal standard (0.60 mg cyclohexanol) and relaxation reagent (0.53 mg Cr(acac)₃) were added as 150 uL in the same solvent mixture. The phosphitylating reagent used was

2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane and was added to the lignin solution just prior to being analyzed (50 uL). The spectrometer (Bruker 400 MHz DMX) recording conditions used were exactly as described in the literature (45° pulse, 25 sec pulse delay, 10,000 Hz sweep width, 200 transients, and using an inverse gated decoupling pulse sequence).

Quantitative ¹³C-NMR

Quantitative ¹³C-NMR experiments were performed following literature procedures (7). Roughly 100 mg of the residual lignin sample was dissolved into ~0.6ml of DMSO-d₆ and filtered into a 5 mm nmr tube. All spectra were recorded at 50°C using a Bruker 400 MHz DMX instrument. Typical recording conditions were employed (90 pulse, 10 sec pulse delay, 25,000 Hz sweep width, 8000-16,000 transients, and using an inverse gated decoupling pulse sequence).

RESULTS AND DISCUSSION

Bleachability of Kraft Pulps

Five pulps were delignified in a D(EO) sequence. These were conventional kraft (CK) pulps having unbleached kappa numbers of 28.0 and 18.5 (designated C28 and C18) and simulated EMCC® pulps having kappa numbers of 29.1, 18.5 and 14.5 (designated E29, E18, and E14). Duplicate samples of each pulp were independently bleached. The averaged data are summarized in Table 2 and discussed below with reference to how bleachability is affected by reducing the unbleached kappa number and differences in bleachability between conventional and EMCC® pulps.

Table 2. Bleachability parameters for conventional and EMCC® pulps.

Parameter	Conventional		EMCC®		
Unbleached Kappa No.	28.0	18.5	29.1	18.5	14.5
Kappa No. after D	11.0	9.6	11.0	7.5	6.0
TAC/ΔKappa	0.30	0.38	0.30	0.31	0.33
Kappa No. after (EO)	3.8	3.8	3.3	3.0	2.3
TAC/ΔKappa	0.21	0.23	0.21	0.22	0.23
Brightness after (EO)	47.4	49.9	49.8	50.2	53.5

Delignification in the D stage.

The ClO₂ consumption per unit of kappa number reduction increased as the kappa number of the conventional kraft pulps was decreased. Expressed as TAC per unit of kappa number reduction, it was 0.30 for the 28 kappa pulp, increasing to 0.38 at 18.5 kappa. In the case of the EMCC®

pulps, TAC consumption per unit of kappa number reduction in the D stage was only increased from 0.30 to 0.33 when the kappa number was decreased from 29 to 14. When the unbleached kappa number was 18.5, significantly more lignin was removed from the EMCC® pulp than from the CK pulp. This difference between CK and EMCC® pulps at low kappa numbers is of interest inasmuch as it suggests that there are important structural differences between the two types of residual lignin, even though the kappa numbers are more similar after a subsequent oxidative extraction stage, as discussed below.

Delignification in the D(EO) partial sequence.

For both pulp types, TAC consumption per unit of kappa number reduction increased slightly as unbleached kappa number decreased. Brightness increased slightly, and in the case of the EMCC® pulps, the kappa number after the extraction stage decreased significantly, from 3.3 at 29 kappa to 2.3 at 14.5 kappa.

Summary of observations on bleachability.

Decreasing unbleached kappa number does not seriously impair the bleachability of either CK or EMCC® pulps. There is, however, a slight increase in ClO₂ consumption per unit of kappa number reduction in both the D and D(EO) stages. At a given unbl. kappa no., EMCC® is more readily delignified in the D(EO) stages than CK, resulting in a slightly lower overall chemical requirement for EMCC®.

Residual Lignin Structure

The bleaching studies serve to illustrate the dependence of bleaching efficiency on the kraft pulping process. Studies by Yamasaki, Gellerstedt, Hortling, and others have begun to explore the nature of residual lignin in kraft pulps and its dependency upon pulping procedures and how it is degraded during bleaching (9,11,12,13,14,15). To determine if the bleachability results observed in this paper are dependent upon the chemical structure of the residual lignin present in the pulp we elected to isolate samples of lignin from each pulp and characterize these materials by employing advanced NMR methods.

Lignin samples from the three EMCC® kraft pulps, the two CK pulps, and one additional low kappa kraft pulp (CK of kappa 13, designated C13) were isolated employing an acid hydrolysis procedure (11,14). In this manner pulp samples were acid hydrolyzed with a 9:1 mixture of dioxane/water for one hour. After work-up the lignin samples were freeze-dried and collected as a fine powder. The resulting material was analyzed by elemental analysis, ¹³C-NMR and ³¹P-NMR of phosphorylated lignin samples. Table 3 summarizes the

results of elemental analysis. Although limited structural data can be inferred from these measurements it is interesting to note the differences in H content for the EMCC® and conventional kraft pulps. The lower lignin conventional and EMCC® kraft pulps exhibited increasing amounts of sulfur for the lower kappa number pulps. The methoxyl contents for the EMCC® pulps appear to decrease with kappa number, whereas the methoxyl content of the conventional kraft pulps was relatively insensitive to the extent of delignification.

Table 3. Methoxyl and elemental analysis of isolated residual lignin.

Lignin ID	C	H	O	S	OCH ₃
C28	100	97.2	31.5	0.83	6.20
C18	100	92.3	30.6	1.07	6.26
C13	100	90.5	33.6	1.08	6.46
E29	100	92.7	30.7	0.95	7.17
E18	100	92.9	30.3	1.09	7.23
E14	100	92.8	30.9	1.62	6.50

Lignin ID's are designated by the first letter of the cook type followed by the kappa number.

¹³C-NMR analysis of residual lignins.

Of the many spectroscopic methods available to characterize lignin, few have been shown to be as versatile as ¹³C-NMR. Fundamental studies now permit routine analysis of lignin functional groups employing modern NMR spectrometers (7,16,17). The lignin samples isolated from pulp were characterized following published quantitative ¹³C-NMR procedures (7). Figure 1 provides representative spectral data for the residual lignins isolated from the high and low kappa number EMCC® kraft pulps. Of the various lignin functional groups that can be characterized by this technique some of the more notable functional groups include substituted and unsubstituted aromatic carbons (δ 160-122 and 122-106 ppm, respectively); C_β of β-O-4 aryl ether units and C_α in β-5 and β-β units (δ 90-78 ppm); γ-carbon of arylglycerol β-aryl ether structures (δ 61-57 ppm); and the methylene signal of the diarylmethane unit (δ 29-27 ppm). These signals are of interest since they provide a facile means of measuring the amounts of condensed lignin and β-O-4 and other aryl ether linkages remaining in the pulps (7,17).

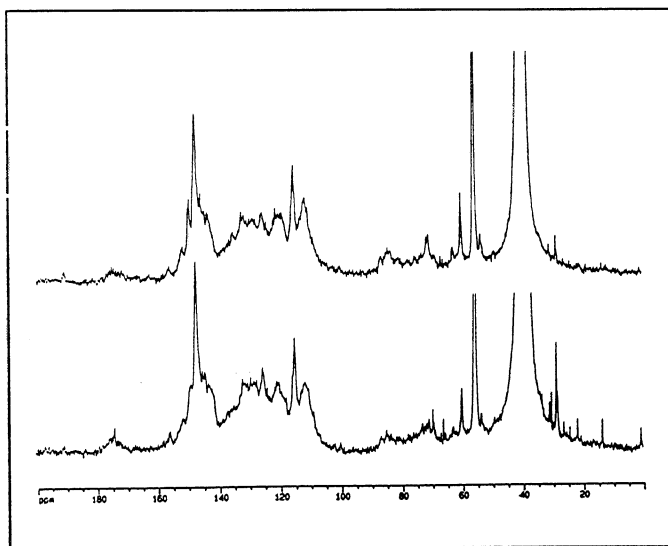


Figure 1. ^{13}C -NMR spectra recorded under 'quantitative' conditions for 29 kappa EMCC® (upper) and 14 kappa EMCC® (lower) residual lignins.

Table 4 summarizes the changes in these functional groups for the various isolated residual lignins. The data are expressed as number of carbons per aromatic unit. This was calculated by integrating the aromatic region of the spectra and assigning this region a value of six. All other signals are integrated with respect to this value. The data of Table 4 reveal some interesting differences between the residual lignins analyzed. The amount of substituted aromatic units in the residual lignin increases as the kappa number is decreased for both the conventional and EMCC® kraft pulps, suggesting that the lower kappa number pulps contain more condensed structures. A comparison between the conventional and EMCC® residual lignins shows that the conventional residual lignin, at both high and low kappa numbers, contains more condensed type structures. The content of a particular condensed diarylmethane structure containing a methylene group was also quantified and found to increase with decreasing kappa number. This structure is formed by the condensation reaction between formaldehyde and two phenolic units (18). The formation of formaldehyde comes about by the loss of γ carbons containing a primary hydroxyl group. The loss of such structures is also indicated by the ^{13}C -NMR analysis.

The ^{13}C -NMR analysis also showed that the content of aryl ether linkages decrease with kappa number. The content of such structures was found to be highest in the EMCC® pulp with a 29 kappa number, substantially higher than the 28 kappa conventional. The content of these structures are reduced upon further delignification. Differences in the content of these structures between conventional and EMCC® residual lignins also reduce at lower kappa numbers.

Table 4. ^{13}C -NMR quantitative analysis of residual lignins isolated from kraft pulps. The numbers are expressed per aromatic unit (17).

Lignin ID	Aromatic carbons		Aliphatic carbons linked to oxygen		-CH ₂ -diarylmethane
	sub.	unsub.	C α , C β *	C γ **	
C28	4.07	1.93	0.29	0.19	0.08
C18	4.21	1.79	0.31	0.18	0.13
C13	4.22	1.78	0.25	0.15	0.17
E29	3.87	2.13	0.35	0.20	0.07
E18	4.12	1.88	0.30	0.18	0.12
E14	4.12	1.88	0.25	0.16	0.16

*C α in β -5 and β - β ; and C β in β -O-4 structures

** C β in arylglycerol β -O-4 structures

^{31}P -NMR analysis of residual lignin.

Recently, derivatization of lignin with selective phosphitylation reagents coupled with ^{31}P -NMR analysis has been shown to be a very effective method for characterizing residual lignin. This procedure was initially employed to detect ortho-quinones in mechanical pulps (19) but has now been further developed by Argyropoulos as a versatile and effective means of quantifying the content of various hydroxyl groups present in lignin including primary, secondary (both erythro and threo forms of β -O-4 structures), and aromatic (guaiacyl and condensed/biphenolic) hydroxyl groups depending on the derivatizing reagent used (6,10,20,21,22). Employing this technique the residual lignin samples were derivatized with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane and analyzed by quantitative ^{31}P -NMR. Figure 2 illustrates the spectral information acquired for the low and high lignin content conventional kraft pulps. The results from analyzing the six residual lignin samples in this manner are summarized in Figures 3,4,5 and 6.

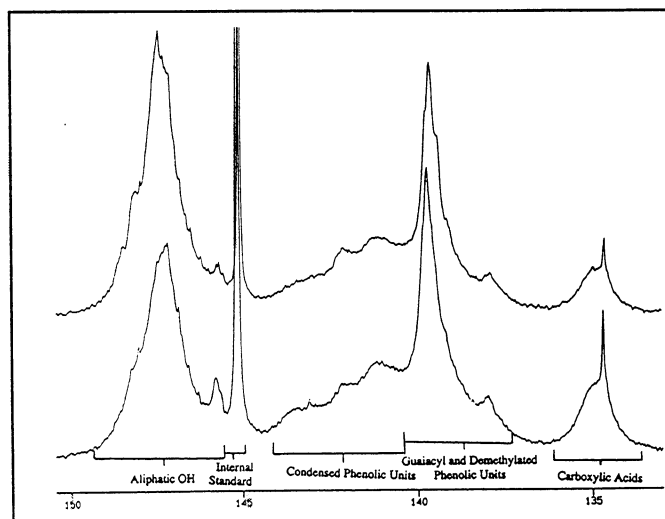


Figure 2. ^{31}P -NMR spectra of 29 kappa EMCC® (upper) and 14 kappa EMCC® (lower) residual lignins derivatized with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane.

The changes in residual lignin carboxylic acid content are plotted in Figure 3. The results indicate a continuing enrichment of carboxylic acid groups in the residual lignins as the kappa number of the pulps is decreased for both the EMCC[®] and conventional kraft pulps. Conventional kraft pulping appears to afford slightly greater amounts of carboxylic acids in the residual lignins.

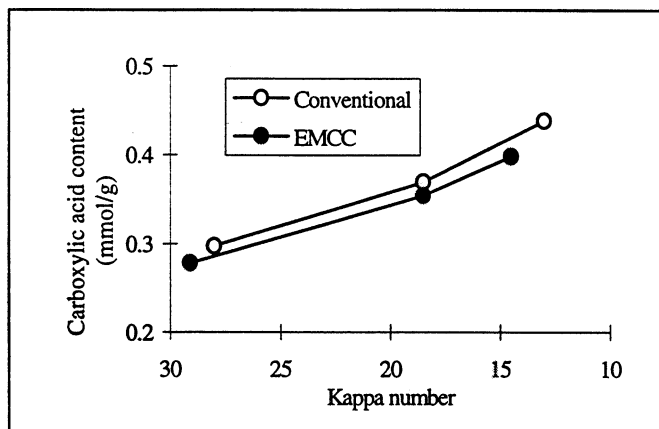


Figure 3. Carboxylic acid content of residual lignin samples isolated from EMCC[®] and conventional kraft pulps as determined by ³¹P-NMR analysis.

Figures 4, 5 and 6 are plots of phenolic content versus kappa numbers for the various residual lignins. With respect to bleaching chemistry of chlorine dioxide, changes in phenolic content of the residual lignin is of great interest since chlorine dioxide is particularly reactive towards such structures. Figure 4 is a plot of the total phenolic content versus the kappa number. As shown in Figure 4, the total phenolic content of the residual lignins isolated from pulps with kappa numbers greater than 28 are comparable, regardless of the pulping process. The data from the CK pulps indicate that the total phenolic content initially increases on going from kappa number 28 to 18 and then levels off. The EMCC[®] pulps, on the other hand, appears to yield a lignin that has an increasing phenolic content as the extent of delignification increases. The overall trend in increased phenolic content upon extended delignification has been previously noted by Lai et al. (23).

The total phenolic content is composed of two types of phenolic units, condensed and uncondensed guaiacyl units, each of which can be accurately quantified by ³¹P-NMR. Figure 5 is a plot of the uncondensed (or guaiacyl) phenolic content versus kappa number for the various residual lignin samples. The plot shows that as the kappa number is decreased, the guaiacyl phenolic content of the EMCC[®] residual lignins continues to increase while that of the CK residual lignins increases over the kappa number range from 28 to 18 but then levels off. Figure 6 shows that for the EMCC[®] residual lignins the content of condensed phenolic

units continues to increase with decreasing kappa number while the content of such structures levels off in the CK pulps.

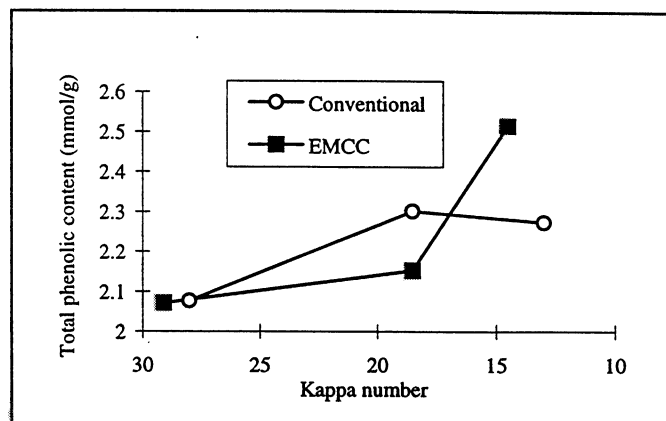


Figure 4. Total phenolic content of residual lignin samples isolated from conventional and EMCC[®] kraft pulps as determined by ³¹P-NMR analysis.

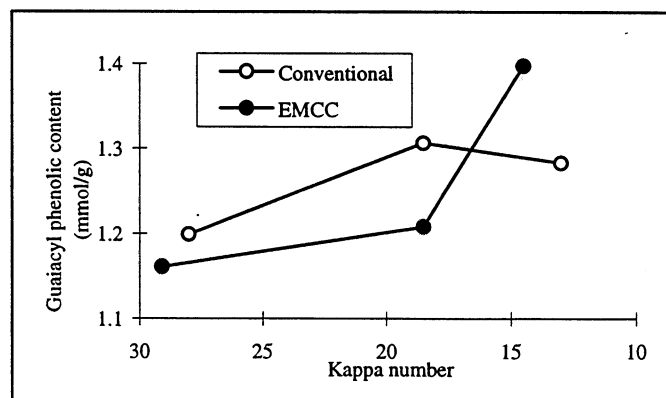


Figure 5. Guaiacyl phenolic content of residual lignin samples isolated from conventional and EMCC[®] kraft pulps as determined by ³¹P-NMR analysis.

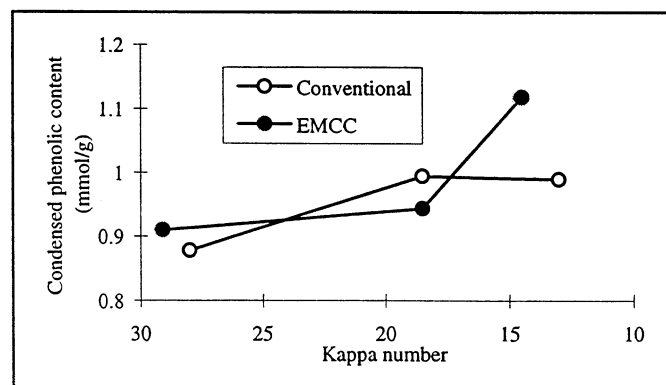


Figure 6. Condensed phenolic content of residual lignin samples isolated from conventional and EMCC[®] kraft pulps as determined by ³¹P-NMR analysis.

Summary of spectroscopic studies of unbleached residual lignins and relationship to pulp bleachability.

The ^{13}C -NMR results show that as the kappa number is decreased for both conventional and EMCC[®] pulps there is a decrease in etherified linkages in the residual lignin structure, most of which can probably be assigned to aryl ether linkages. The results also show that more substituted aromatic carbons are found in the residual lignins as the kappa number is decreased. This result was substantiated by the ^{31}P -NMR analysis which showed that during both conventional and EMCC[®] pulping, condensed phenolic units increase in the residual lignin as kappa number is decreased. Although the ^{31}P -NMR data confirmed the ^{13}C -NMR data, the ^{13}C -NMR data has the advantage of analyzing all structural information, not just the hydroxyl groups. The increase in condensed type lignin observed by the ^{13}C -NMR data could therefore be a combination of phenolic and non-phenolic structures. The ^{31}P -NMR data also suggested that the phenolic content of the EMCC[®] residual lignins continued to increase with decreasing kappa number while for the CK residual lignins the phenolic content leveled off after an 18 kappa. At low kappa numbers the EMCC[®] residual lignin contains more phenolic structures (both condensed and uncondensed) than the CK residual lignin.

The observed changes in phenolic concentration does not correlate with the bleachability of these pulps during the D and (EO) stages, even though phenolic structures are believed to be the main reactive site for ClO_2 (1,25). The bleaching study showed that for all pulps the ClO_2 requirement per unit kappa number reduction was higher for pulps of lower unbleached kappa number despite their higher contents of phenolic groups. The phenolic content of the residual lignin seems not to be simply related to the bleachability with ClO_2 . On the other hand there appears to be a positive correlation between bleachability and the content of aryl ether linkages or condensed structures or both. Although condensed phenolic groups are readily attacked by ClO_2 (24,26) condensed non phenolic structures may represent an obstacle to ClO_2 delignification.

Chemical Reactivity of Residual Lignin with Chlorine Dioxide

To further explore the fundamental bleaching chemistry of the lignin present in these pulps, the residual lignin samples isolated from both EMCC[®] pulps and CK pulps were treated with chlorine dioxide in an aqueous dioxane (9:1 dioxane:water) solution. After reacting with the ClO_2 for 30 minutes, the solvent was removed and the oxidized residual lignin samples phosphitylated and re-examined by ^{31}P -NMR. This technique was first used by Sun and Argyropoulos in their investigation of the reactivity of residual lignin towards

ClO_2 (24). Table 5 summarizes the changes in guaiacyl and condensed phenolic groups and carboxylic acid groups. The depletion and introduction of such groups are expressed as a percentage of the original (unbleached) amount. The charge of ClO_2 used in these experiments corresponded to a 0.05 kappa factor.

Table 5. Change in content of various functional groups in residual lignins upon treatment with a charge of chlorine dioxide equivalent to a 0.05 kappa factor (expressed as a percentage of the original content).

Lignin ID	Condensed -OH	Guaiacyl -OH	COOH
C28	-23.5	-25.5	60.9
C18	-24.9	-24.1	37.9
C13	-26.3	-27.3	38.8
E29	-28.9	-27.7	80.2
E18	-27.4	-29.2	42.1
E14	-29.3	-29.1	36.2

An analysis of the change in phenolic groups shows that such groups are readily degraded during the reaction with ClO_2 . There was no preference given towards the type of phenolic groups the ClO_2 reacted with as suggested by the similarity in the percent decrease for both types of phenolic groups. The residual lignin isolated from the EMCC[®] pulps appeared to exhibit slightly higher losses of phenolic groups compared to the CK residual lignins.

Table 5 also monitors the introduction of carboxylic acids into the residual lignin. This functional group is of great interest since its introduction into the residual lignin can be related to the efficiency of the oxidant which can be further related to the observed bleaching response (9). The results show that the higher kappa EMCC[®] and CK residual lignins yield significantly higher amounts of carboxylic acid groups than lower kappa residual lignin. Again the EMCC[®] residual lignin seems to be slightly more reactive towards the ClO_2 than the CK residual lignin, particularly at the higher kappa number as a greater percentage of carboxylic acids were introduced into this lignin.

The formation of carboxylic acids under acidic conditions with ClO_2 is believed to occur mainly via the oxidation of phenolic structures, although the possibility of introducing carboxylic acids into non-phenolic aromatic units has also been suggested (27). The introduction of a greater amount of acids and a depletion of a similar amount of phenolic structures in the higher kappa residual lignin compared to the lower kappa residual lignins, for both conventional and EMCC[®] lignin, is interesting. Even though the lower kappa number residual lignins had a higher content of phenolic units, the higher kappa residual lignins introduced more carboxylic acids. This is further evidence for the role of aryl ether

linkages and/or condensed structures as being determinants for bleachability. Non-phenolic aryl ether structures, present in smaller amount at lower kappa number, can also react with ClO_2 to form acids, and may be responsible for the increased formation of acids at higher kappa number. The less condensed type structure in the residual lignin of higher kappa pulp may also aid in the formation of carboxylic acids. Condensed non-phenolic structures may be less reactive towards the ClO_2 .

Oxidative degradation of non-phenolic structures may also occur by elemental chlorine and its equilibrium partner hypochlorous acid (27,28). Hypochlorous acid is known to be formed during ClO_2 bleaching thus its reaction with non-phenolic structures cannot be ruled out as possibly contributing to the carboxylic acid group formation (29).

SUMMARY AND CONCLUSIONS

The bleachability of conventional and EMCC® kraft pulps in a D(EO) sequence has been related to the residual lignin structure and its reactivity towards ClO_2 . During the delignification stages (D and D(EO)) the ClO_2 consumption per unit kappa number reduction increased slightly as the kappa numbers of both the CK and EMCC® pulps decreased. This result suggests that the higher kappa number pulps contain residual lignin that is more reactive towards the ClO_2 . Analysis of the residual lignin structure suggested that the content of free phenolic structures could not be simply related to this result, since the lower kappa number pulps had a higher content of phenolic structures. The structural analysis revealed that the higher kappa number pulps had a higher content of aryl ether linkages and a lower content of condensed structures, possibly including condensed non-phenolic structures. The higher content of aryl ether linkages and lower amounts of condensed structure suggests that such a lignin may be more reactive towards ClO_2 . Experiments in which the isolated residual lignins were reacted with ClO_2 showed that the higher kappa number residual lignins, in spite of their lower phenolic content, had a larger increase in carboxylic acid formation, suggesting a more reactive lignin. The bleachability experiments also showed that EMCC® pulps were more readily delignified in the D(EO) stages than the CK pulps, resulting in a slightly lower overall chemical requirement for EMCC®. The residual lignin reactivity experiments suggested that the EMCC® pulp residual lignin was slightly more reactive than the CK residual lignin, which is consistent with the bleachability result.

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